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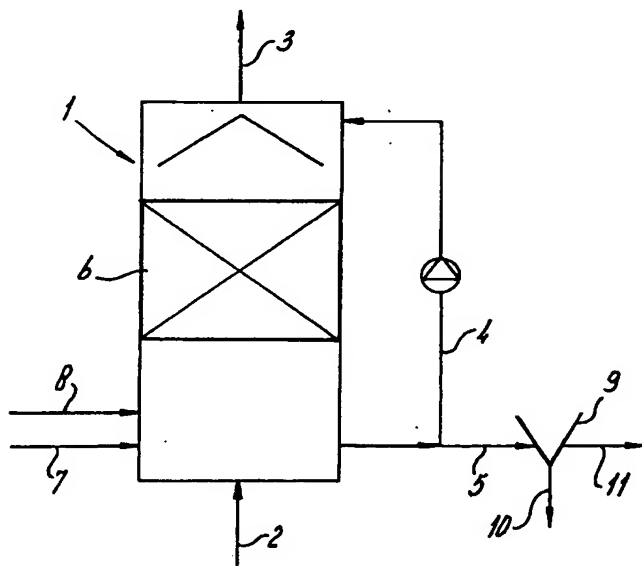
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(54) Process for biological removal of sulphide

(57) The invention provides a process for the removal of sulphides from a gas stream by scrubbing the gas with an aqueous washing liquid and treating the washing liquid with sulphide-oxidising bacteria in the presence of an electron acceptor and reusing the treated liquid as a washing liquid, wherein the scrubbing and the bacterial treatment are carried out in the same reactor and nitrate is used as the electron acceptor. The process is especially useful for desulphurising natural gas at high pressure.



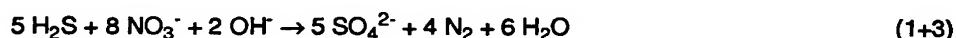
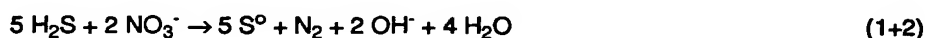
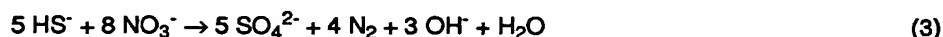
Description

The present invention relates to a process for the removal of sulphides from a gas stream by scrubbing the gas with an aqueous washing liquid and treating the spent washing liquid with sulphide-oxidising bacteria in the presence of an electron acceptor in a reactor and recycling the treated liquid as a washing liquid.

Such a process is known e.g. from WO 92/10270, WO 94/29227 and WO 96/30110. In these prior art processes oxygen is used as an electron acceptor. The oxygen is fed at a limited rate so as to direct the oxidation of sulphide to elemental sulphur rather than to sulphate. The use of oxygen as an electron acceptor, however, requires the presence of an aeration system including a compressor, pipings, spargers, and in most cases a separate reactor. The investment costs for such a system are relatively high, especially when small volumes of water or gas are to be treated or when e.g. high-pressure natural gas is to be desulphurised.

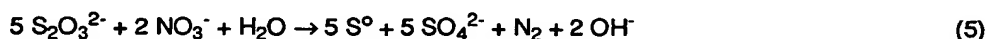
According to the invention, the spent sulphide-containing washing liquid is treated with sulphide-oxidising bacteria in an integrated scrubber/bioreactor, using nitrate as an electron acceptor.

The biological oxidation reactions of hydrogen sulphide by colourless sulphur bacteria, such as the genus *Thiobacillus*, especially the species *T. denitrificans*, using nitrate as an electron acceptor are the following:



Reaction (1) denotes a preliminary reaction, e.g. occurring in a gas scrubber, wherein gaseous hydrogen sulphide is dissolved as hydrosulphide anions. Reaction (2) describes the anoxic oxidation of sulphide to elemental sulphur, whereas reaction (3) represents the complete oxidation of sulphide to sulphuric acid. Reaction (1+2) is the total net reaction of hydrogen sulphide to elemental sulphur.

The reactions involving oxidation of thiosulphate with nitrate as electron acceptor are the following:



Nitrate can be added as a solid salt, but preferably it is added as a concentrated solution of e.g. potassium nitrate, or a mixture of a nitrate salt and nitric acid. As the conversion of H_2S to elemental sulphur produces alkali (equation 1+2), and the conversion of H_2S to sulphate consumes the same amount of alkali (equation 1+3), acid (preferably nitric acid replacing part of the nitrate) should be added in the preferred case where sulphide is predominantly converted to sulphur. Preferably, nitrate (and nitric acid) is added in a substantially stoichiometric amount for oxidation of sulphide predominantly to sulphur, i.e. about 0.4 mole of nitrate per mole of H_2S , optionally allowing for minor oxidation to sulphate, i.e. 0.4-0.9, especially 0.4-0.6 mole of nitrate per mole of H_2S . An overdosis of nitrate should be avoided, because it destabilises the process due to an accumulation of nitrite (NO_2^-). The nitrite concentration should remain below 1 mM, preferably below 0.5 mM.

The nitrate addition can be controlled using the redox potential of the aqueous solution, as described in EP 96202138.2. Thus the redox potential of the medium of the oxidation is adjusted at a value below -150 mV (against an Ag/AgCl reference electrode), especially below -250 mV. The preferred redox potential range is from -300 to -390 mV, more preferably from -320 to -360 mV (against an Ag/AgCl reference electrode). The range of -300/-390 mV against Ag/AgCl corresponds to a range of -97/-187 mV against a H_2 reference electrode at 30°C. The redox setpoint values apply for a temperature of 30°C and a pH of 8.

The temperature of the biological oxidation is between 10 and 85°C, the optimum being between 20 and 50°C, especially at about 30°C. The optimum pH is in the range of 7-9.

If the solution does not contain nutrients, as is the case with gas scrubbing, these have to be supplied as well. This can be done at the same time as the nitrate supply. The electric conductivity of the washing liquid is preferably kept between 30 and 100 mS/cm.

The bacteria to be used in the present process can be taken from conventional sulphide-oxidising cultures. The bacteria are preferably neutrophilic bacteria and will typically include *Thiobacillus* species, especially *T. denitrificans*.

The process of the invention can be used for treating gases also containing carbon dioxide. The carbon dioxide contributes to the H_2S loading capacity of the scrubbing liquid, especially at high pressures. As an example, the H_2S loading capacity of a scrubbing liquid for scrubbing a pressurised gas (95 bar) having a CO_2 content of 1.1 vol.% is 200 to 300 g/m³. Also the carbon dioxide can be used as a carbon source for the sulphide-oxidising bacteria.

In the process of the invention for the removal of hydrogen sulphide from gas streams, the solution is recycled after oxidation of the sulphide to elemental sulphur, using the same reactor for scrubbing and for anoxic biological treatment. No liquid recirculation between different pressures is necessary. Further advantages are that the equipment can be relatively simple and inexpensive, and that the recycle ratio and thus the liquid residence time can be high so that any loss of biomass is compensated by bacterial growth. If required, the bacteria can be immobilised on a carrier, which carrier can be combined with a packing material in the scrubber. For a simple operation such immobilisation can be omitted.

The process can be performed in an installation as depicted in the figure. According to this figure, a gas scrubber/reactor 1 is equipped with a sulphide-containing gas supply 2 and a purified gas exit 3. Washing liquid is recycled through 4 without pressure difference and surplus liquid is drawn off at 5. The scrubber contains a packing material 6 for improving contact between gas and washing liquid. Make-up water, containing nutrients and trace elements, is introduced through line 7. Nitrate (electron acceptor) is supplied through 8, but may also be added to the make-up water in 7. Nitric acid can be used for pH control and be added through 7 or 8 or separately. A separator 9 is disposed in bleed stream 5, where a sulphur slurry is separated off and discharged through 10. The clarified liquid 11 can be reused as make-up water at 7. As an alternative, a sulphur separator may be placed in recycle loop 4. Preferably the elemental sulphur is not completely separated: a residual level of 0.1-5 wt.%, especially 0.3-3 wt.% is advantageous for enhanced sulphide absorption by the washing liquid and improved buffering. The sulphur level in the scrubber/reactor can be adjusted by adjusting the recycle ratio (flow 4 vs. flow 5) and/or by adjusting the separation efficacy of the sulphur separator.

The process of the invention can be advantageously applied for the treatment of small biogas streams, such as those producing less than 100 kg of sulphur per day. For such streams, the cost for the addition of nitrate is more than compensated by the savings on investment as a result of the omission of expensive compressors, spargers and other devices necessary for oxygen supply.

The process of the invention is also suitable for the treatment of natural gas of high pressure, e.g. 50 bar or higher. These high pressures normally make biological treatment of natural gas unattractive, because of the high energy consumption resulting from pressurising the washing liquid for entering the gas scrubber and depressurising the liquid for entering the aerated aerobic reactor. Prior art processes for removal of hydrogen sulphide from natural gas include: (1) reversible chemical or physical absorption based on alkanolamine or carbonate solvents; these processes require high temperatures and pressure differences; also part of the expensive amine solution is lost with the bleed stream; (2) direct conversion through absorption and oxidation, e.g. based on a redox reaction between H_2S and Fe^{3+} , wherein the reduced metal is reoxidised with oxygen; drawbacks of such processes are the tendency of plugging with sulphur solids and the use of expensive, corrosive metal chelates; (3) non-regenerative absorption, wherein hydrogen sulphide is absorbed onto, e.g., active carbon or iron sponges, which are regularly replaced and disposed ("throw away").

In the present process the pressurising/depressurising steps can be eliminated, since the biological treatment does not require oxygen gas, and the gas scrubbing can thus be integrated with the bioreactor.

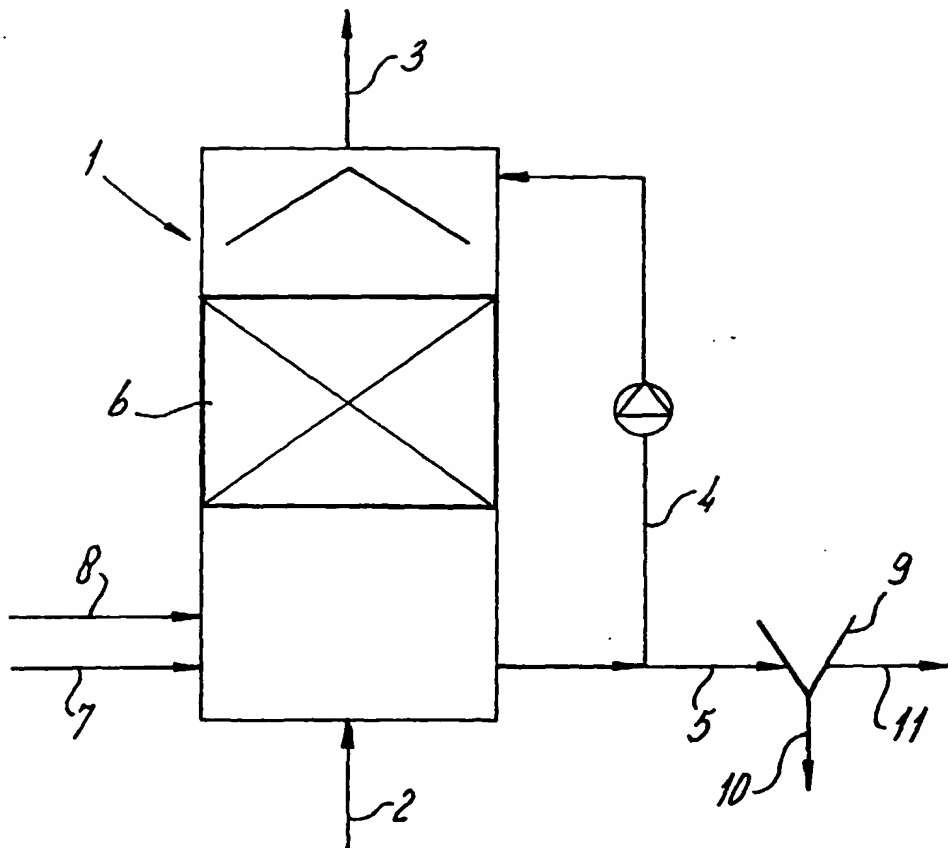
Example

In an installation as depicted in figure 1 having a scrubber volume of 10 m³, natural gas at 95 bar containing 100 ppmv of H_2S and 1.1 vol.% of CO_2 is treated at 25,000 Nm³/day, using a scrubbing liquid having a pH of about 8.5 and using a biomass containing *Thiobacillus denitrificans*. Potassium nitrate and nitric acid are fed at 50-200 g/hr and 50-200 g/hr, respectively. A liquid recycle rate of 0.5-5 m³/hr is used. The H_2S content of the purified gas is 2 ppmv (desulphurisation efficacy: 98%).

Claims

1. Process for the removal of sulphides from a gas stream by scrubbing the gas with an aqueous washing liquid and treating the washing liquid with sulphide-oxidising bacteria in the presence of an electron acceptor and reusing the treated liquid as a washing liquid, characterised in that the scrubbing and the bacterial treatment are carried out in the same reactor and nitrate is used as the electron acceptor.
2. Process according to claim 1, wherein the sulphide is oxidised to elemental sulphur using a stoichiometrical amount of nitrate.

3. Process according to claim 2, wherein the elemental sulphur is partly removed from the treated liquid in such a way that a residual level of sulphur of 0.1-5 wt.% remains.
4. Process according to any one of claims 1-3, wherein the specific conductivity of the washing liquid is between 30 and 100 mS/cm.
5. Process according to any one of claims 1-4, wherein neutrophilic sulphide-oxidising bacteria are used.
6. Process according to any one of claims 1-5, wherein the pH of the washing liquid is between 7 and 9.
7. Process according to any one of claims 1-6, wherein the gas stream also contains carbon dioxide.
8. Process according to any one of claims 1-7, wherein the gas stream is natural gas having a pressure of at least 50 bar.





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EUROPEAN SEARCH REPORT

Application Number
EP 96 20 3347

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y,D	WO 96 30110 A (PACQUES BV ;BUISMAN CEES JAN NICO (NL)) 3 October 1996 * page 4, line 26 - line 29 * * page 5, line 1 - page 6, line 7; claims; figures *	1-7	B01D53/84 C10L3/10
Y	EP 0 472 249 A (PREUSSAG NOELL WASSERTECHNIK G) 26 February 1992 * the whole document *	1-3,5-7	
Y	WO 93 24416 A (PACQUES BV ;BUISMAN CEES JAN NICO (NL)) 9 December 1993 * page 6, line 4 - line 10 *	4	
A	WO 91 18661 A (ABB ENVIRONMENTAL SERVICES INC) 12 December 1991 * page 1, line 1 - line 8 * * page 2, line 15 - line 26 * * page 6, line 26 - line 30 *	1-3,5,6	
A	US 5 236 677 A (TORRES-CARDONA MARIO D ET AL) 17 August 1993 * column 3, line 16 - column 4, line 63; figure 1 *	1-3,5	TECHNICAL FIELDS SEARCHED (Int.Cl.6) B01D C01B C10L
A	EP 0 224 889 A (IMHAUSEN CHEMIE GMBH) 10 June 1987 * claims 1-11; figures 1-3 *	1,2,5,6	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24 April 1997	Examiner Eijkenboom, A
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document</p>			

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